

Excess Volume of Mixing for Binary Mixtures of Some Nitroalkanes and Symmetrical Aromatic Hydrocarbons

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The excess volume of mixing (V^E) for the binary mixtures of the nitroalkanes nitromethane, nitroethane, and 2-nitropropane with symmetrical aromatic hydrocarbons benzene, *p*-xylene, and mesitylene has been determined by density measurements at 293.15 K. The V^E values are positive over the whole mole fraction range except those for the mixtures of nitroethane and 2-nitropropane with benzene and *p*-xylene where they are negative at lower and positive at higher mole fractions of nitroalkanes. The results have been discussed in terms of dipole-induced dipole electrostatic molecular interactions significantly affected by steric factors.

Introduction

Various excess properties (1-6) like the excess Gibbs free energy, excess enthalpy, excess volume, etc. have been helpful in the study of molecular interactions in binary liquid mixtures. In our earlier publications the dielectric constants (7) and viscosities (8) of nitroalkanes and non-polar aromatic hydrocarbons have been studied. The nitroalkane series show a distinct trend of their dipole moments. Aromatic hydrocarbons with different polarizabilities and progressively overcrowded steric environments were chosen as the second component to study the effect of the interactions between dipoles and sterically hindered polarizable compounds. In this paper excess volumes of nine binary systems between nitromethane, nitroethane, and 2-nitropropane + each of the nonpolar liquids benzene, *p*-xylene, and mesitylene are reported.

Experimental Section

Nitromethane (BDH, LR), nitroethane (BDH, LR), 2-nitropropane (E. Merck), benzene (Sarabhai Merck, spectroscopic grade), *p*-xylene (E. Merck), and mesitylene (E. Merck) were used. All the chemicals except spectroscopic grade benzene were purified (8) before use, and their purity was checked by measuring densities at 293.15 K which are compared with the literature values (Weast, R. C. *Handbook of Chemistry and Physics*; Chemical Rubber Co.: Cleveland, OH, 1971) as follows:

	exptl value	lit. value
benzene	0.8792	0.87865
<i>p</i> -xylene	0.8613	0.8611
mesitylene	0.8651	0.8652
nitromethane	1.1310	1.1371
nitroethane	1.0478	
2-nitropropane	0.9891	0.9876

A series of solutions covering the complete mole fraction range were prepared gravimetrically by injecting compo-

nent liquids with a syringe into vials sealed with rubber to avoid evaporation losses. Densities of the liquids and liquid mixtures were measured with a single-stem capillary pycnometer after equilibrating in a thermostat regulated at 293.15 K. The densities were accurate to ± 0.0001 g cm⁻³. The excess volumes for the binary mixtures were calculated from the density values of the pure liquids and liquid mixtures with an accuracy of ± 0.001 cm³ mol⁻¹.

Results and Discussion

The density of the mixture (ρ_{12}) and excess volume of mixing (V^E) as a function of composition for the systems studied at 293.15 K are given in Table 1. The V^E values for each binary system are fitted to the following equation by the method of least squares to correlate the composition dependence of V^E :

$$V^E/(\text{cm}^3 \text{ mol}^{-1}) = x_1 x_2 [v_0 + v_1(x_1 - x_2) + v_2(x_1 - x_2)^2] \quad (1)$$

where v_0 , v_1 , and v_2 are the constants for the binary systems and x_1 and x_2 are the mole fractions of components 1 and 2, respectively. The constants v_0 , v_1 , and v_2 together with the standard deviation $\sigma(v^E)$ are recorded in Table 2.

Powell and Swinton (9) suggested that the large positive V^E values indicate the weak unlike interaction where as large negative V^E values usually show the presence of strong interaction to form an intermolecular complex. The positive values of V^E for the whole composition range in most of the systems studied except the binary mixtures of nitroethane and 2-nitropropane with benzene and *p*-xylene show the presence of weak forces between unlike pairs of molecules. The V^E values for the binary systems nitroethane and 2-nitropropane with benzene and *p*-xylene are negative at lower concentration and positive at higher concentration of nitroalkanes. The positive values of V^E for nitromethane with benzene at 293.15 K by Suri et al. (10) have also been reported using the dilatometric technique which are quite in line with our observations. The V^E values of Marsh (11) measured by a continuous dilution dilatometer for the binary mixtures of purified nitromethane with benzene and *p*-xylene at 298.15 K and of Nigam et

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Table 1. Densities (ρ_{12}) and Excess Volumes of Mixing (V^E) at 293.15 K

x_2	$\rho_{12}/$ (g cm ⁻³)	$V^E/$ (cm ³ mol ⁻¹)	x_2	$\rho_{12}/$ (g cm ⁻³)	$V^E/$ (cm ³ mol ⁻¹)
Benzene (1) + Nitromethane (2)					
0.0000	0.8792		0.4940	0.9705	0.180
0.0919	0.8932	0.056	0.7053	1.0259	0.155
0.2238	0.9153	0.126	0.8004	1.0556	0.122
0.2978	0.9289	0.159	0.9073	1.0942	0.029
0.3994	0.9494	0.177	1.0000	1.1310	
<i>p</i> -Xylene (1) + Nitromethane (2)					
0.0000	0.8613		0.6051	0.9672	0.201
0.1151	0.8754	0.057	0.6915	0.9925	0.181
0.1918	0.8859	0.093	0.7940	1.0284	0.149
0.2724	0.8984	0.103	0.8837	1.0677	0.056
0.4256	0.9256	0.179	1.0000	1.1310	
0.4810	0.9368	0.225			
Mesitylene (1) + Nitromethane (2)					
0.0000	0.8651		0.6061	0.9599	0.426
0.1192	0.8775	0.129	0.7112	0.9904	0.372
0.2056	0.8880	0.207	0.7985	1.0217	0.3190
0.3019	0.9010	0.295	0.8912	1.0644	0.179
0.3858	0.9140	0.378	1.0000	1.1310	
0.4761	0.9306	0.410			
Benzene (1) + Nitroethane (2)					
0.0000	0.8792		0.5827	0.9683	0.016
0.0901	0.8917	-0.003	0.6952	0.9882	0.017
0.1956	0.9068	0.004	0.7869	1.0054	0.001
0.2856	0.9202	0.009	0.8790	1.0233	-0.006
0.3897	0.9364	0.009	1.0000	1.0478	
0.4893	0.9524	0.024			
<i>p</i> -Xylene (1) + Nitroethane (2)					
0.0000	0.8613		0.6083	0.9496	0.017
0.0968	0.8723	-0.009	0.6994	0.9683	0.019
0.1917	0.8839	-0.001	0.7938	0.9900	0.016
0.3000	0.8986	-0.013	0.9011	1.0182	-0.002
0.4039	0.9140	-0.001	1.0000	1.0478	
0.4953	0.9290	0.004			
Mesitylene (1) + Nitroethane (2)					
0.0000	0.8651		0.6112	0.9445	0.248
0.0912	0.8739	0.029	0.6912	0.9605	0.239
0.1908	0.8844	0.072	0.7813	0.9810	0.222
0.2974	0.8968	0.137	0.8874	1.0099	0.143
0.3871	0.9087	0.159	1.0000	1.0478	
0.5179	0.9282	0.227			
Benzene (1) + 2-Nitropropane (2)					
0.0000	0.8792		0.5981	0.9453	0.001
0.0983	0.8903	-0.016	0.7032	0.9566	0.020
0.2123	0.9030	-0.021	0.7847	0.9656	0.011
0.2863	0.9113	-0.031	0.9080	0.9792	-0.005
0.4048	0.9243	-0.023	1.0000	0.9891	
0.5002	0.9348	-0.023			
<i>p</i> -Xylene (1) + 2-Nitropropane (2)					
0.0000	0.8613		0.6039	0.9288	-0.015
0.1052	0.8716	-0.026	0.7089	0.9431	0.004
0.2079	0.8822	-0.044	0.8008	0.9566	0.007
0.2945	0.8915	-0.041	0.8925	0.9710	0.004
0.3973	0.9032	-0.042	1.0000	0.9891	
0.4976	0.9153	-0.039			
Mesitylene (1) + 2-Nitropropane (2)					
0.0000	0.8651		0.6007	0.9246	0.206
0.0955	0.8729	0.022	0.7022	0.9381	0.221
0.1983	0.8820	0.035	0.8014	0.9530	0.191
0.2994	0.8914	0.085	0.8980	0.9693	0.131
0.4005	0.9015	0.143	1.0000	0.9891	
0.5048	0.9131	0.169			

al. (12) at 318.15 K are also positive. The excess volumes of nitroethane with benzene and *p*-xylene and of 2-nitropropane with benzene by Marsh et al. (11, 13) at 298.15 K are negative at lower mole fractions and positive at higher mole fractions of nitroalkanes. The trend of V^E values for these mixtures at 293.15 K in our case is also the same except a very few stray values. As the V^E values are very much affected by the temperature, the comparison of our

Table 2. Values of the Constants v_0 , v_1 , and v_2 of Eq 1 and Standard Deviations $\sigma(V^E)$ for the Various Systems at 293.15 K

system	$v_0/$ (cm ³ mol ⁻¹)	$v_1/$ (cm ³ mol ⁻¹)	$v_2/$ (cm ³ mol ⁻¹)	$\sigma(V^E)/$ (cm ³ mol ⁻¹)
nitromethane + benzene	0.7804	0.0960	-0.3401	0.017
nitromethane + <i>p</i> -xylene	0.8310	-0.1259	-0.4203	0.025
nitromethane + mesitylene	1.6792	-0.4822	-0.2383	0.010
nitroethane + benzene	0.0802	0.0025	-0.1959	0.005
nitroethane + <i>p</i> -xylene	0.0230	-0.0757	-0.0858	0.009
nitroethane + mesitylene	0.8745	-0.6839	0.0569	0.007
2-nitropropane + benzene	-0.0160	-0.1314	-0.1331	0.012
2-nitropropane + <i>p</i> -xylene	-0.1192	-0.2245	0.0164	0.006
2-nitropropane + mesitylene	0.6885	-0.7654	0.2066	0.008

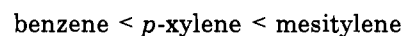
Table 3. Gas-Phase Dipole Moment (μ_{gas}) of Nitroalkanes

nitroalkane	$\mu_{\text{gas}}^a/\text{D}$
nitromethane	3.46
nitroethane	3.65
2-nitropropane	3.73

^a Reference 7.

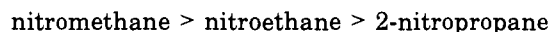
V^E values with those of other researchers at different temperatures is not possible.

The magnitude of the V^E values of nitromethane in the three aromatic hydrocarbons follows the trend



which indicates that interaction between unlike pairs of molecules decreases as benzene is replaced by *p*-xylene and mesitylene, respectively. A similar trend is observed in the case of nitroethane and 2-nitropropane with the exception of the binary mixture of *p*-xylene.

A perusal of Table 1 shows that for a common aromatic hydrocarbon the V^E values are in the following order for different nitroalkanes:



The above order of V^E values shows that the interaction becomes gradually stronger between unlike pairs of molecules from nitromethane to 2-nitropropane. This is quite in line with the gas-phase dipole moment values of the polar molecules which are lowest for nitromethane and greatest for 2-nitropropane as given in Table 3. Thus, the excess volume measurement also provides a similar conclusion which was obtained by previous studies (7, 8) for these systems.

It appears logical to propose that when polar nitroalkane comes in close proximity with the aromatic hydrocarbon, it induces a dipole moment in the latter, resulting in a dipole-induced dipole electrostatic attraction.

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